EVALUATING VPT2 SCHEMES FOR ACCURATE AUTOMATED THERMOCHEMISTRY AND SPECTROSCOPY FOR NON-COVALENT SYSTEMS

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High level computational thermochemical protocols take an additive approach to computing the total energy of a molecular system. For small systems, components related to the electronic structure can be systematically converged using methods such as coupled-cluster theory at the complete basis limit. The vibrational level pattern (and at 0 K the zero-point energy, ZPE) yields a relatively large contribution and is thus a possible source of significant error. An inaccurate ZPE leads to poor quantities such as enthalpies of formation and hence interpretations in kinetics and dynamics. As a result an accurate determination of this one term is critical and the focus of this talk. Accurate anharmonic models such as VPT2 and VCI exist for semi-rigid molecules in the gas phase. Non-covalent systems are also of importance in a wide range of areas. The VPT2 model has not been applied as widely to non-covalent systems and questions remain as to its general applicability. Here, a screening of low-cost implementations of VPT2 calculations were performed for a series of vdW systems as large as Benzene-Ar. The screening was done with an automated thermochemical protocol. Comparisons are made with full-dimensional variational calculations using global potential energy surfaces, and to experimental data where available.